

Polar Smectic Films

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We report on a new experimental procedure for forming and studying polar smectic liquid crystal films. A free standing smectic film is put in contact with a liquid drop, so that the film has one liquid crystal/air interface and one liquid crystal/liquid interface. This polar environment results in changes in the textures observed in the film, including a boojum texture and a previously unobserved spiral texture in which the winding direction of the spiral reverses at a finite radius from its center. Some aspects of these textures are explained by the presence of a K_{sb} -term in the bulk elastic free energy that favors a combination of splay and bend deformations.

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When considering soft-condensed-matter composed of organic molecules, interfaces have a strong influence on the molecular arrangement within the sample. This is particularly true for thin films (from a few to a few hundred nanometers thick) where the interface contributions are not overwhelmed by the bulk contributions. Thus, thin ordered films are a good probe to investigate the consequences for the molecular arrangement when an asymmetrical environment is imposed on the sample. A polar geometry can be obtained when the film is placed between two different isotropic media: liquid at one interface and air at the other. Illustrations include bi-phasic systems, *e.g.*, pre-wetting films induced on top of a drop of mesogenic liquid [2], as well as bi-chemical systems where the liquid medium is no longer a melted form of the ordered wetting phase but is of a different chemical nature. Focusing on bi-chemical systems, recent work involves nematic films spread on glycerin [3], as well as Langmuir multi-layer [4] and mono-layer [5] films spread on water. Here, the molecular head-tail asymmetry combined with a 2-dimensional confinement (a circular domain within the film) is the source of rich and complex molecular patterns, of which one called a boojum has generated much interest in recent years [6].

In this Letter, we report a new experimental approach to achieve an asymmetric environment using free standing films of smectic liquid-crystal (LC) material, deposited onto a liquid drop by contact. This method makes use of much simpler techniques and smaller scale apparatus than the ones commonly used to study Langmuir films, for example. It also provides researchers with a broad range of experimental possibilities such as wetting the film with any kind of liquid as long as it does not dissolve the liquid crystal, and choosing the initial thickness of the film. Motivated by the rich range of pattern formation in free standing smectic films, we developed this technique especially to study the changes in pattern formation when a free standing film was put into a po-

lar environment. With that in mind, we examined polar films of the tilted chiral smectic C* (Sm C*) phase of several liquid crystals on a variety of liquid substrates. We paid particular attention to single 2D confined domains in which we observed significant changes in the textures involving a topological point defect, including a boojum pattern and, most remarkably, a spiral pattern reversing its direction of winding at a particular radius.

Our samples are obtained starting from a free standing thermotropic smectic film, formed by spreading the smectic across a circular frame (a 6 mm diameter hole in a thin metal plate). The film consists of a stack of molecular layers, each about 30 Å thick, oriented parallel to the two free surfaces in contact with air, defining a film of homogeneous thickness. Using a micrometer screw, the film is slowly lowered toward the top of a liquid drop. The drop (of, say, water) is held in place in a small hydrophilic circle on an otherwise hydrophobically treated glass substrate. When the contact is established, a polar film with one LC/air interface and one LC/liquid interface is formed on top of the drop. The resulting sample consists of the polar film itself as shown in Fig. 1 and of the “remaining” free standing film stretched between the film holder and the liquid medium.

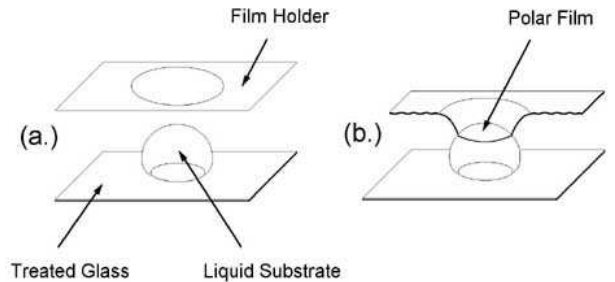


FIG. 1. Experimental set-up: (a) Before contact, a free standing film is spread on the holder and a drop of liquid is deposited on the slide. (b) After contact, the polar film is created on top of the drop.

On the drop, a circular meniscus of extra LC material forms at the junction of the free standing film with the polar film. Depending on the relative surface tensions of the three surfaces meeting at this meniscus, the top of the drop is flatter than initially, still tending to be somewhat curved. The diameter of the polar film can be varied by raising or lowering the film holder position. The original free standing film can be made in thicknesses ranging from thousands down to two layers [7].

We made samples of hundreds of layers as well as of about 30 layers. Extremely thin samples are difficult to deposit by this method. We examined films on distilled water, ethylene glycol, and aqueous solutions of Poly-Vinyl-Alcohol (PVA) and Sodium Dodecyl Sulfate (SDS). We ran the experiment at 20° Celsius in order to minimize the evaporation of the wetting liquid. Most of our studies were made on films of the room temperature ferroelectric Sm C* mixture CS1015 from Chisso [8]. Sm C* is a layered liquid crystal phase composed of chiral (non-reflection symmetric) molecules. The mean molecular long axis, given by the director \hat{n} , chosen to point “upwards” from the film, is tilted relative to the layer normal through an equilibrium angle ψ (26 degrees for CS1015). The projection of \hat{n} onto the plane of the film defines the unit vector field, the c -director $\hat{c}(x, y)$. The chirality of Sm C* results in a spontaneous rotation of \hat{c} as a function of z , the direction normal to the plane of the film. Given the helix pitch of the Sm C* phase for CS1015 of 3 μm , and our maximum film thickness of a few hundred nm, we neglect this effect and we consider $\hat{c}(x, y)$ uniform along z [9].

The samples were examined both under a polarizing transmission microscope (PTM) to study the texture of the c -director, and under a white light reflection microscope to observe their thickness. The images were recorded by a CCD camera and image processing hardware to amplify small differences of intensity. With crossed polarizers, the film image in the PTM is marked by dark brushes when $\hat{c}(x, y)$ is parallel to either polarizer, and by bright brushes when \hat{c} is at an intermediate orientation. Thus, a cross-shaped four-arm extinction pattern corresponds to a 45 degree rotation of \hat{c} between dark and bright areas [10]. However, because we slightly uncrossed the polarizers in order to increase the light intensity, the dark/bright sequence in Fig. 2 and Fig. 3 corresponds to a 90 degree rotation of \hat{c} .

Many interesting effects can occur in thin film samples, including surface induced phase transitions, and superficial ordering different from that in the interior of the film. In the experiments described here, our observation of rapid fluctuations of the c -director in all cases convinced us that samples were in the Sm C* phase. Therefore we analyzed all our observations in the thin film limit, in which film properties are considered uniform in the z direction, resulting from an average of molecular interactions at the surfaces and in the interior of the film.

In particular, both surfaces of a film are naturally polar. In a free standing film, because of the top-bottom symmetry, the opposite polarities of the two surfaces average to zero, while in our samples this symmetry is broken, resulting in a net polarity of the film. However, the net polarity arises only from the surface layers, so the strength of the polar effects is inversely proportional to the sample thickness, making that a useful variable for tuning polarity.

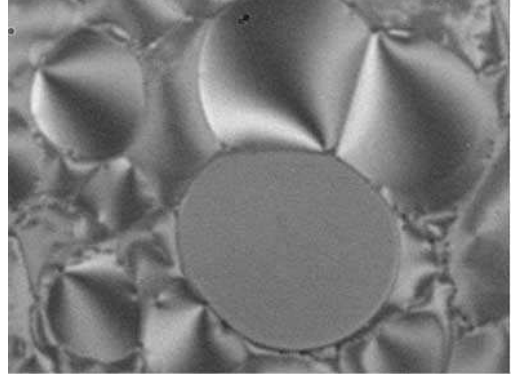


FIG. 2. Polar smectic C* film observed between slightly uncrossed (vertical and horizontal) polarizers. The texture shown in the roughly circular domains, a boojum, is the most commonly observed one. The grey area is a thin (tens of layers) Smectic A domain. Image width: 156 μm .



FIG. 3. Reversing-spiral pattern observed in a polar film between slightly uncrossed (vertical and horizontal) polarizers. Image width: 156 μm .

Our general observations are summarized as follows. Ordinary free standing films of CS1015 exhibit a smectic C* phase for all film thicknesses. The liquid contact induces a non-tilted Smectic A phase [11] for extremely thin films, while thicker films remain in the tilted Sm C* phase. Polar films on water, ethylene glycol and PVA solutions behave similarly, but on SDS solutions we found only the smectic A phase, perhaps due to the entry of SDS into the film.

Upon forming the polar film, we see a multitude of edge

dislocation loops fixing domains of different thickness throughout the area of the film (Fig. 2). These defects, roughly circular, are practically static. This is different from what is observed in newly formed free standing smectic films [12], which steadily evolve toward a uniform film thickness. Moreover, the domains are not isolated from each other, but are packed together, so they resemble a foam, rather than free circular regions. Within a single domain we can compare the texture of the c -director to that observed in the circular islands (thicker regions) seen in free standing films.

The circular topology of a domain, together with a strong anchoring of the c -director at a fixed angle relative to the boundary, combine to produce a topological constraint, resulting in the existence of a point defect in the domain, around which the c -director rotates once. The detailed texture within the domain is dictated by the free energy for the c -director, including anchoring energies at the outer boundary and at the point defect, and the curvature elastic energy for gradients of the c -director within the domain. The free energy expression for the c -director field contains terms consistent with the symmetry of the film. The coefficients of the polar terms should vary inversely with film thickness, and all the coefficients should depend on the average tilt angle of the director \hat{n} in the Sm C* phase. Because the texture minimizing the free energy depends on a competition among different terms, we expect to see different characteristic textures for different samples.

Following the detailed symmetry analysis presented by Langer and Sethna [13], the elastic free energy F for the c -director in a topologically circular domain of a chiral polar Sm C* thin film has the form

$$F = \int_{Area} dA [K_s(\nabla \cdot \hat{c})^2 + K_{sb}(\nabla \cdot \hat{c})(\nabla \times \hat{c}) + K_b(\nabla \times \hat{c})^2] \\ + \oint_{Boundary} dl [\lambda_s(\hat{c} \cdot \hat{m}) + \lambda_b(\hat{c} \times \hat{m})],$$

in which K_s and K_b are the familiar splay and bend curvature elastic constants, λ_s and λ_b give the strength of the lowest order terms dictating the c -director anchoring at the domain boundary, and \hat{m} is the outward normal to the boundary. For 2D vectors, the \times operation produces a scalar. In addition to the requirement that K_s and K_b be positive, to make the free energy density positive definite for arbitrary values of splay and bend, we require that $K_{sb}^2 < 4K_sK_b$. The K_s and K_b terms could have been written to include spontaneous splay and bend in the ground state [14], but those added terms can be integrated by parts to combine with the λ_s and λ_b terms.

For a free standing film, which is not polar, the K_{sb} and λ_s terms are absent from the free energy. The λ_b term favors one direction of tangential orientation of the c -director at the boundary of the island. If $K_b < K_s$

[15], then a simple minimum energy texture is one of pure bend, with azimuthal orientation of \hat{c} , within the circle, and the point defect at its center. This highly symmetric texture, often seen in islands on free standing films [16], is characterized by a cross-shaped four-brush extinction pattern with straight arms, when viewed between crossed polarizers [10].

In the case of a polar film, this simple texture is no longer observed, and other textures of the same topology are seen, the boojum texture (Fig. 2) with a point defect located at the edge of the domain and straight brushes emerging radially from the defect, and several different spiral textures, including the “reversing spiral” (Fig. 3) with a centered defect around which the c -director field winds first one way and then the other, as a function of radius. In thinner films, the boojum texture is the most common, while spirals are seen in thicker samples; this may reflect differences in the strength of the polar perturbation. To understand certain aspects of these textures, we look to the broken polar symmetry. The free energy expression above for the polar films contains two terms (K_{sb} and λ_s) that break symmetry in different ways.

First, the λ_s term in the boundary energy combines with the λ_b term to favor one oblique orientation angle ϕ^* of the c -director relative to a domain boundary, rather than tangential or normal orientation. This oblique boundary condition is clearly seen in the boojum domains of Fig. 2, where dark brushes, corresponding to loci of constant \hat{c} , meet the circumference where it is oriented obliquely, rather than horizontally or vertically.

Second, the K_{sb} term, discussed first by Langer and Sethna [13], appears only with both chiral and polar symmetry. This term lowers the symmetry of a texture because it favors combined splay and bend deformations. For a circular island with a centered point defect at $r = 0$, instead of pure splay or pure bend being the lowest energy distortion, a particular ratio of splay to bend minimizes the energy. In the absence of boundary anchoring conditions, this would lead to a simple spiral texture, with the c -director making a constant angle $\phi = \phi_{sb}$ (or $\phi_{sb} + \pi$), with respect to the radial vector throughout the domain.

Combining these two symmetry breaking effects, it is clear why various spiral patterns are observed when the point defect is centered in a domain of a polar chiral film. At the outer boundary of the domain, the c -director is anchored at some angle $\phi^* = \phi_b$. At the inner boundary defined by the point defect, the anchoring angle is $\phi^* = \phi_d$, which need not be the same as ϕ_b . Simultaneously, away from the boundaries, ϕ would tend to approach ϕ_{sb} . The energy minimizing texture requires that ϕ is a function of radius r in the domain. To find this functional dependence, one can make a transformation $\xi = \ln(r/\epsilon)$, where ϵ is the core radius of the defect. The problem then maps onto that of a strip of Sm C* in the (ξ, η) -plane contained between two parallel lines at which the boundary conditions on ϕ are ϕ_d and ϕ_b respectively,

with an applied uniform magnetic field at angle ϕ_{sb} relative to the normal to the strip. The director tends to lie parallel to the magnetic field, and the strength of the effective field coupling depends on relative magnitudes of the elastic constants. Often, this leads to solutions in which ϕ varies monotonically across the strip, corresponding to ordinary spirals for the brushes observed in our experiments. However, much as in the well-studied Fredericks transition in nematic layers [11], the solution can involve ϕ first rotating in one direction (from ϕ_d toward ϕ_{sb}) as a function of ξ , reaching an extremum, and then rotating in the other direction to match the second boundary condition, ϕ_b . This produces the reversing spiral observed in Fig. 3.

The straight brushes emerging from the defect in the boojum texture (Fig. 2) are in contrast to the spiral patterns described above. Clearly the c -director does not have a constant orientation angle ϕ_d at the inner boundary around the point defect. Ignoring anchoring effects at that inner boundary, one can find an energy minimizing solution which produces the observed straight brushes and constant ϕ_b at the outer boundary. In terms of polar coordinates (r, θ) centered on the point defect, and ϕ again an angle relative to the radial vector, a stable solution is $\phi = \theta + \phi_b$, independent of r . This solution, in a circular domain of radius R centered at the point $(R, 0)$ remarkably has the fixed angle ϕ_b between \hat{c} and \hat{m} at all points on the boundary of the domain. This is just the structure we see, subject to perturbations from the non-circular shape of the domains.

This boojum is similar to the topological defect texture observed in isolated domains of other systems like Langmuir monolayers on water [17], which are also polar, and islands of the Smectic I phase in an otherwise Smectic C free standing film [13]. In those systems the anchoring of the c -director at the lateral boundary is weak, and the topological defect is “expelled” from the domain. This lowers the free energy by removing the high elastic strain near the defect as well as its core energy, and by replacing it with a lower energy that results from the violation of the boundary anchoring in a small region. However, in our polar films, the boundary anchoring of the c -director is apparently stronger, and the defect appears to be right at the edge of the domain. We speculate that this strong anchoring results from the large change in layer thickness at the domain boundaries of our polar films. Why the defect is attached to the boundary is not known, but it probably involves the energetics of the defect core structure.

In conclusion, we have developed a novel technique for studying polar smectic liquid crystal films, and have observed novel textures in smectic C* films in a polar environment. The strength of the polar perturbation can be changed by varying the film thickness. We have shown through a free energy analysis that important aspects of the changes in texture relative to ordinary free standing

smectic C* films are a direct consequence of the polar symmetry of the films. In connection with the studies reported here, we have also observed reversing spirals and other textural novelties in circular islands on non-polar free standing Sm C and Sm C* films, which will be discussed elsewhere.

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